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The effect of functionalized carbon nanotubes on thermal-mechanical performance of Epoxy nanocomposite coatings

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ABSTRACT : *The new approaches for preparing nanocomposite coating by modificated carbon nanonotubes (CNTs) and epoxy resin was done in the study. thermal-mechanical performance of nanocomposite coating was investigated and the results were reported in this paper. The physic-chemical techniques such as Differential scanning calorimetry (DSC) and Thermal gravimetric analysis (TGA) were used to characterize the thermal performance of Epoxy nanocomposite coating. The test techniques for mechanical properties of paint coating as adhesion, hardness, impact resistance and bending strength were employed in the work. The results indicated that CNTs were dispersed in epoxy coating with only ratio of 0.1 wt% enhanced the Glass Transition Temperature (Tg), decomposition temperature of epoxy coating and improved mechanical properties significantly. Also functionalized CNTs can be reinforced thermal-mechanical of the epoxy coating better than neat CNTs.*
Keywords:

I. INTRODUCTION

Polymer nanocomposites are constructed by dispersing a filler material into nanoparticles that form flat platelets. Nanoparticles allow for much lower loading levels than traditional fillers to achieve optimum performance. Usually addition levels of nanofillers are less than 1%, which significantly impact weight reduction of nanocomposite films. Organic coatings provide protection either by a barrier action from the layer or from active corrosion inhibition provided by pigments in the coating [1]. Nanocomposite coating systems are defined by generic type of binder or resin, and are grouped according to the curing or hardening mechanism of that generic type and additional nanofillers. The organic binder or resin of the coating material is primarily responsible for determining the properties and resistances of the paint [3]. Epoxy resins are known for their excellent properties of anti-corrosion and of chemical resistance [2]. When properly co-polymerized with other resins (particularly those of the amine or polyamine family) or esterified with fatty acids, epoxy resins will form a durable protective coating [4]. However, organic materials alone cannot be used for high-performance applications because of their limited properties. Consequently, the addition of fillers that can withstand high temperatures, such as carbon black, silicone, and silica is frequently employed into the epoxy paint system to overcome restraint [5]. Therefore, this work used nanocarbon materials to fill in epoxy binder for protective coatings application for steel surfaces. Carbon nanotubes is a 1D structure type of nanocarbons, which offer superb electrical and thermal conductivity properties [6]. Recently, CNTs have been used efficiently in numerous research works to significantly enhance the mechanical properties of composites. With their amazing mechanical properties and exceptionally high aspect ratios, nanocarbons (NCs) are seen as one of the most beneficial nanomaterials for nano-reinforcement [6,7].

II. MATERIALS

In this study, Carbon nanotubes material was producted by Bao Lam Khoa company (Da Nang, Vietnam). Epotec YD 011X-75 is a solution of unmodified low molecular weight solid diglycidyl ether of bisphenol-A resin in xylene. The dissolution of Epotec YD 011 in xylene facilitates handling. Epotec TH 7515 is a high viscosity reactive polyamide used as a curing agent for liquid or solution grade epoxy resins such as Epotec YD 515 or Epotec YD 011X75 to produce thermoset adhesives and coatings; organic solvents including: aceton, etanol, n-butanol, toluene (Merk). They are produced by Xilong Chemical Factory and Guangdong GuanghuaSci-Tech Co.

III. METHODS

Characterization methods of the nanocarbon materials : In this work, Fourier Transform Infrared spectroscopy (FTIR) was employed to characterize functionalized carbon nanotubes. A Thermo Nicolet 6700 spectrometer was used to collect the FTIR data for chemical structure analysis of the fillers. The crystal structure characterization of them were analyzed by X-ray diffraction (XRD) and performed using a Siemens D5005 X-ray diffractometer.

Preparation of steel substrate surface : The adhesion of the coating depend on the preparation of the surface. The preparation is often referred to as pretreatment. The used samples are Q-Panel standard steel panels with their dimension depends on testing properties. The surface pretreatment was done according to three– stages procedure as follows:

Stage 1 – Abrading by mechanical method as a sanding to remove dirt, rust, oxides...
Stage 2 – Cleaning by hand wiping with an organic solvent as acetone, ethanol, n-butanol for 5 minutes at ambient temperature to remove abrasion dust.
Stage 3 – Drying in the vacuum dryer for 10 minutes at 50 ºC. They were kept in plastic bags at room temperature for coating of the paint.

Dispertion the nanocarbon materials in the epoxy binder : The dispersion of CNTs is one of the key factors that strongly influence the properties of nanocomposites. There are chemical and physical methods for nanopartical materials dispersion. The nanocarbon materials were used to disperse in epoxy resin with a content ratio of 0.1 wt%. At first, the nanocarbon materials were disperse in epoxy binder by a sonication bar (Sonic VC 750) for 1h until becoming the good dispersion.

Preparation of the nanocomposite coating samples on the steel surface for tests : Before coating the the dispersed mixture on the steel surface, the curing agent (calculated weight ratio of 10:1 on the epoxy binder) was added into the mixture. Following this, incorporating them evenly was carried by the stirrer bar. Because of curing reaction of the mixture at room temperature, so that coatings on the prepared substrate surfaces was done by a spray gun immediately after mixing. The finally, the promotion was carried for fully cured the epoxy coating at room temperature for 7 days. The test samples were formed for examination of physico-mechanical and anti-corrosion properties. Dry film thickness of the samples was about 20-30 µm.

The methods for thermal properties characterizations of polymers : Two methods were employed to characterize thermal performances of nanocomposite coating in this work. They are Differential scanning calorimetry (DSC) and Thermal gravimetric analysis techniques (TGA). DSC is employed on a Mettler Toledo (Germany) to measure glass transition temperatures, crystalline phase transition temperatures, crystalline phase transformation temperatures and melting point temperatures by ASTM E1545. TGA is used to measure weight loss upon heating to evaluate the thermal stability and susceptibility to temperature decomposition [5] and was carried out on a Labasys Evo TG-DTA 1600 (Setaram, France) by ASTM Standard E164. The test samples were heated in the nitrogen atmosphere at a rate of 10 ºC/min.

The mechanical properties techniques of nanocomposite paint coatings [2] In the study, the physico-mechanical properties tests of the films were chosen to investigate properties of nanocomposite coatings based on the epoxy resin and the nanocarbon materials are listed below:

- Adhesion: The cross-cut test is a simple and easily practicable method for evaluating the adhesion of single- or multi-coat systems The standard ASTM D 3359-97 test is used; a numerical rating system from 1-mark for total failure to 5-marks scale may be used to evaluate tape adhesion test results. The test is operated using aslicer’s instrument of Sheen (England).
- Hardness: Performed according to ASTM D3363 via a pencil method and using a Wolff-Wilborn Pencil Tester which includes 20 pens corresponding from 6B to 6H scale. It is usually used to measure resistance to indentation by a series of increasingly hard pencils that have been sharpened to a chisel point.
- Bending strength: Determined according to ASTM D522, the data was collected using Sheen's 809 device.
- Impact resistance: A way to measure impact resistance is ASTM D2794-93 was used, a standard weight is dropped from a height onto a coated panel. The indentation is inspected to detect if the coating has cracked. The weight can be dropped from different heights, and the results are then measured in kG.cm unit.

IV. RESULTS AND DISCUSSION

Characterization of the functionalized carbon nanotubes : The functionalized carbon nanotubes (f-CNTs) were characterized by FTIR and XRD methods.

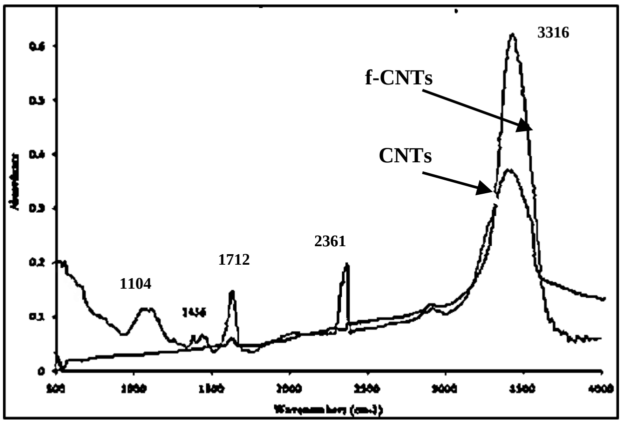


Figure 1. FTIR spectra of CNTs and f-CNTs

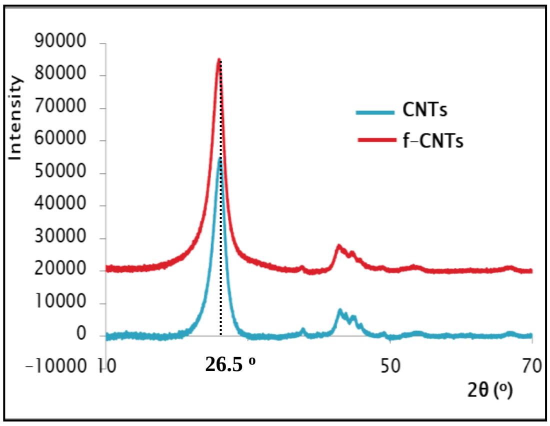


Figure 2. XRD spectra of CNTs and f-CNTs

Table 1. Summary of FTIR spectra on presence of CNTs and f-CNTs

Wavenumber (cm^{-1})	Peak assignment
1104	C-O stretching vibration of carboxyl group or epoxy group
1324	Peak of OH group of carboxylic (COOH)
1712	Peak of C=O bond of carboxylic group
2361	C-C stretching vibration of graphite structure
3316	Peak of OH bond of carboxylic group or of adsorpbed H_2O in samples

The FTIR analysis in Fig.1 and Table.1 was used to approve presence of chemical group containing oxygen of f-CNTs such as –OH, -COO, -CO while CNTs absent them. Also, the Fig.2 was showed the strongest and sharpest diffraction peak at around 2θ = 26.5°, which could be indexed as the reflection of graphite. The sharpness of this peak indicates that the graphite structure of both CNTs and f-CNTs. Due to the CNT's intrinsic nature, the main features of the X-ray diffraction pattern of CNTs are close to those of graphite [8].

4.2. The result of thermal properties tests

The results of DSC analysis were showed in the Fig. 3 and data was analysed and listed in Table 2.

Table 2. The DSC data of samples

Sample	$T_{m\ onset}$ (°C)	$T_{m\ mid}$ (°C)	$T_{g\ onset}$ (°C)	$T_{g\ mid}$ (°C)
Epoxy	90.80	97.95	95.71	89.12
CNTs/Epoxy	93.29	98.79	97.48	93.29
f -CNTs/Epoxy	94.38	103.72	98.06	102.06

$T_{m\ onset}$ - Onset melt temperature; T_{mmid} - Midpoint melt temperature; $T_{g\ onset}$ - Onset glass transition temperature; $T_{g\ mid}$ - Midpoint glass transition temperature

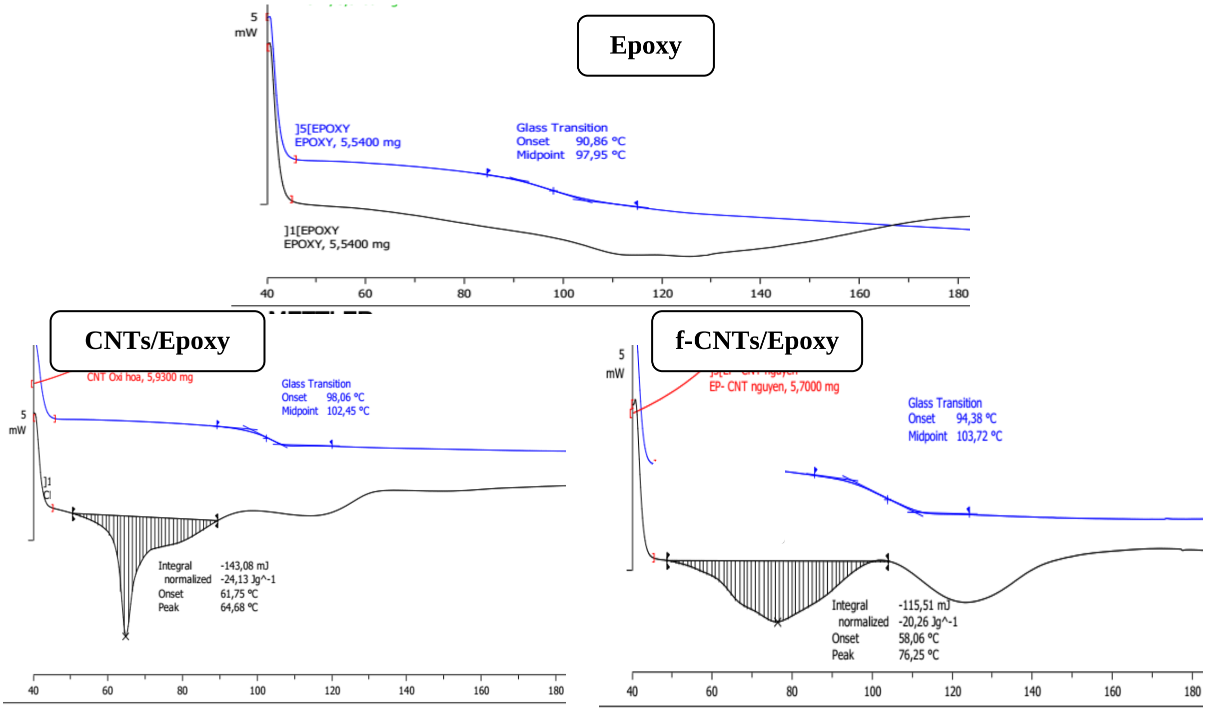
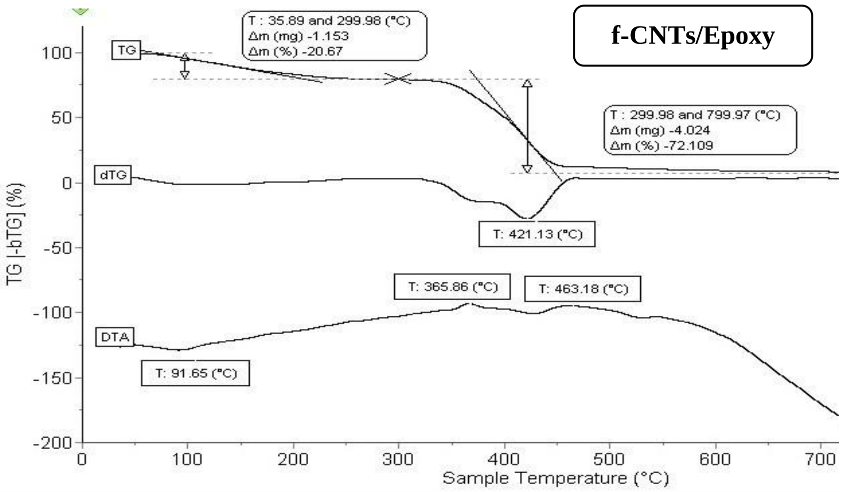


Figure 3. The DSC curves of Epoxy, CNTs/Epoxy and f-CNTs/Epoxy coating samples

The table 2 and table 3 showed that both the glass transition temperature (T_g), melt temperature (T_m) and decomposition temperature (T_d) of epoxy coating were increased with additional CNTs nanofiller. The Fig.3 presented that both T_m and Tg were higher ~ 5ºC for f-CNTs and ~2 ºC than free filler epoxy coating. While the Fig 4 indicated the $T_{d,\ onset}$ of epoxy coating takes place at 328.98 ºC for the pure epoxy, 363.01 ºC for CNTs/Epoxy and 365.86 ºC for the f-CNTs/Epoxy nanocoating, in-dicating that CNTs nanofiller in the epoxy coating increases epoxy resin's thermal stability. Can see that f-CNTs effect on thermal high-performance better more than neat CNTs. This can be explained present of functional groups on f-CNTs surface supported the strong interfacial interaction, which maybe covalent bonds, hydrogen bonds, ion bonds etc., between CNTs nanofiller and epoxy resin matrix. This attributed homogeneous dispersion of CNTs and to improve thermal high-performace of nanocomposite. The good nanofiller dispertion formed strong, compact network polymer structure, so that thermal stability and physic-mechanical properties have been enhanced significantly compared to non-filler epoxy coating [6-8].



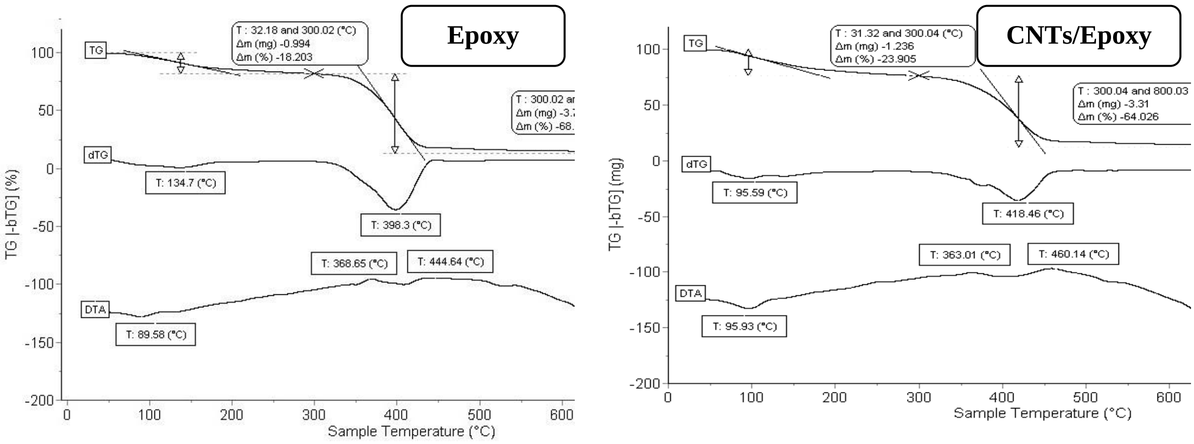


Figure 4. TGA curves of epoxy coating, CNTs/Epoxy and f-CNTs/Epoxy coating samples

Table 3. The TGA data of samples

Sample	**$T_{d\ onset}$**	**T_{dmax} (°C)**	**$T_{d,90\ wt\%}$**
Epoxy	328,98	334,60	366,40
CNTs/Epoxy	363,01	418,46	460,14
f -CNTs/Epoxy	365,86	421,13	463,18

T_{do} - Onset decomposition temperature; $T_{d\ max}$ – The strongest decomposition temperature;
$T_{d,90\ wt\%}$ – Decomposition temperature at maximum loss weight.

The result of physico-mechanical properties tests: Testing physico-mechanical properties is an important part of the operation of a paint coating. Testing is done to monitor the system and to confirm that the paint coatings meets quality standards and the expectations of the customer. Testing of paint coating is used to confirm physico-mechanical properties of the coating after being applied and cured. The used particular tests depend on the properties that the coating has to provide and to respect the established quality standards [8-10]. The results are showed in Table 4.

Table 4. Physico-mechanical and anticorrosion properties of the samples

Properties	**Epoxy**	**CNTs/Epoxy**	**f-CNTs/ Epoxy**	**Unit**	**Standard**
Hardness	HB	1H	1H	Pencil	ASTM D3363
Adhesion	2	1	1	Mark	ASTM D3359
Bending strength	3	2	2	mm	ASTM D522
Impact resistance	50	70	75	kG.cm	ASTM D2794

As can be seen from Table 4, only with the concentration of the nanocarbon materials as low as 0.1wt%, the physico-mechanical properties of epoxy paint coatings have been improved significantly. The properties of nanocomposite samples were better very much than the epoxy coatings samples. This suggested that the addition of carbon nanotructure materials played as a pigment or filler for purposes of a paint coatings. The hardness of both CNTs/Epoxy and f-CNTs/Epoxy nanocomposite coatings (~1H) is higher than that of original epoxy coating (~HB). While the adhesion of epoxy coating samples is the lowest in all. It means that additional CNTs enhanced the hardness and adhesion of Epoxy paint coating.

It is important for features of coatings. The impact resistance is increased 40% for f-CNTs/Epoxy samples and 50% for CNTs/Epoxy sample compared to original epoxy coating samples, respectively. While the bending strength of both f-CNTs/Epoxy and CNTs/Epoxy samples were increased upto ~33.33 % compared to one of original epoxy samples. It is known pigments or fillers are particulate solids that are dispersed in paints to provide certain characteristics to them, including color, opacity, durability, mechanical strength, and corrosion protection for metallic substrates [10-14]. These results indicated that the effect of the functionalized carbon nanotubes on physico-mechanical properties of epoxy coatings better than the CNTs. Therefore, the results able to be explained that the presence of the oxygen containing functional groups of f-CNTs may create covalent bonds with the functional groups of epoxy resin. The covalent bonds have higher energy so that leaded to create strong interfacial bonding between the filler and epoxy resin so that further great distribution and dispersion of f-CNTs compared to neat CNTs. Hence, the effect of f-CNTs nanofiller on physico-mechanical properties and anticorrosion of epoxy paint coatings is higher than those of unmodified CNTs.

V. CONCLUSION

- The physico-mechanical properties of the epoxy coatings have been significantly improved by adding only 0.1 wt% of nanocarbon materials in the epoxy binder notably. This also was presented in increasing the glass transition temperature and melt temperature by DSC analysis data.
- The thermal stability of the CNTs reinforcement epoxy coating was demonstrated by TGA showing greater than **~**40 ºC for f-CNTs and **~** 35 ºC for CNTs increase in decomposition temperature comparing to non-filler epoxy coating. The nanocarbon functionation should be dittributed for developping the high-performances of Epoxy coatings.
- The chemically functionalized CNTs is greatly promised candidate in reinforcement application for nancomposite materials compared to neat CNTs..

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